Process safety and environmental protection. 2008, vol. 86, issue 3, p. 198-207. http://dx.doi.org/10.1016/j.psep.2007.12.002

Modelling Accidental Releases of Dangerous Gases into the Lower Troposphere from Mobile Sources

A. Bernatik[1], W. Zimmerman[2], M. Pitt[2], M. Strizik[1], V. Nevrly[1], Z. Zelinger[3]

[1]*VSB-Technical University of Ostrava, Faculty of Safety Engineering, Lumirova 13, 700 30 Ostrava-Vyskovice, Czech Republic, tel: +420 597 322 833, e-mail: ales.bernatik@vsb.cz*

[2]*University of Sheffield, Department of Chemical and Process Engineering, Mappin Street, Sheffield S1 3JD, United Kingdom*

[3]*J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejskova 3, 182 23 Prague 8, Czech Republic*

Abstract

The article reports the results of different methods of modelling releases and dispersion of dangerous gases or vapours in cases of major accidents from road and rail transportation in urban zones. Transport accidents of dangerous substances are increasingly frequent and can cause serious injuries in densely inhabited areas or pollution of the environment. For quantitative risk assessment and mitigation planning, consequence modelling is necessary.

The modelling of dangerous substance dispersion by standard methods does not fully represent the behaviour of toxic or flammable clouds in obstructed areas such as street canyons. Therefore the predictions from common software packages as ALOHA, EFFECTS, TerEx should be augmented with CFD models or physical modelling in aerodynamic tunnels, and further studies are planned to do this.

The goal of this article is to present the results of the first approach of modelling using these standard methods and to demonstrate the importance of the next development stage in the area of transport accident modelling of releases and dispersions of dangerous substances in urban zones in cases of major accident or terrorist attacks.

Key words: Major Accidents, Transportation of Dangerous Substances, Modelling of Release and Dispersion

1. Introduction

The area of major accident prevention represents a relatively new branch of science. Nevertheless, *transportation* accident prevention requirements are an outgrowth of this branch. The first approach is to evaluate stationary risk sources with the largest amount of dangerous substances. However, dangerous substances limits have been decreased (amendments of SEVESO II Directive) and current attention was moved to so-called “unclassified risk sources” and to mobile risk sources. Greater and greater amounts of dangerous substances are transported by road and rail. The threat of terrorist actions, possibly involving the transport of dangerous substances, has also contributed to interest in this area.

The assessment of mobile risk sources is not yet prescribed by law in the European Union. However the transport of dangerous substances represents a particular hazard above all to the densely populated areas of urban zones, where releases of toxic or flammable substances into the air may endanger the health and/or lives of many inhabitants. To date, the evaluation of the consequences of accidents from mobile risk sources have been dealt with only haphazardly and not in detail.

Information on the spread of atmospheric pollutants above a landscape after accidental releases can be collected by direct measurements of pollutant concentration levels, but only with sparse resolution. The results of mathematical modelling and/or the simulation of atmospheric conditions and the given landscape in an aerodynamic tunnel potentially represent a more comprehensive source of information. To predict the dispersion of toxic substances released into the troposphere as a result of accidents, mathematical modelling is the foremost tool. Some previous studies have compared modelling methods and simulation in case studies, for example study of chlorine releases from water treatment works (comparison of a flat terrain model with CFD model and wind tunnel modelling) (McBride et al., 2001) or CFD modelling of toxic gas dispersion in the vicinity of complex buildings, structures, and topography (comparison of FLACS model with 2D models) (Dharmavaram and Hanna, 2007).

2. Accident history and statistics

In the past, many transport accidents with dangerous substances have occurred worldwide. The following accidents are well known: road accident in Houston, USA in 1976, release of ammonia, 6 people killed, 178 people injured; road accident in San Carlos, Spain in 1978, BLEVE of propylene, 200 people killed; rail accident in Mississauga, Canada, in 1979, BLEVE of LPG and release of chlorine, 200,000 people evacuated; rail accident in Montanas, Mexico in 1981, release of chlorine, 28 people killed, 1000 people injured; and other accidents. From study of 1932 accidents that occurred during the transport of hazardous substances by road and rail the results obtained show an increase in the frequency of accidents over time (Oggero et al., 2006). More than half of the accidents happened on roads (63%). The most frequent accidents were releases (78%), some of which were followed by fires (28%), explosions (14%) and gas clouds (6%).

An example of a more recent accident is the train derailment near Minot, North Dakota (NTSB, 2004). At approximately 1:37 a.m. on January 18, 2002, Canadian Pacific Railway freight train 292-16 derailed 31 of its 112 cars about 1/2 mile west of the city limits of Minot, North Dakota. Five tank cars carrying anhydrous ammonia catastrophically ruptured, and a vapour plume covered the derailment site and surrounding area. One resident was fatally injured, 11 people sustained serious injuries, and 322 people, including the 2 train crewmembers, sustained minor injuries. Damages exceeded $2 million, and more than $8 million has been spent for environmental remediation. Contributing to the severity of the accident was the catastrophic failure of five tank cars and the instantaneous release of approximately 350 tonnes of anhydrous ammonia. A cloud of hydrolyzed ammonia formed almost immediately. This plume rose an estimated 300 feet (90 m) and gradually expanded 5 miles (8 km) downwind of the accident site and over a population of about 11,600 people (NTSB, 2004). Figure 1 shows picture of the accident place and a plan of surrounding area.

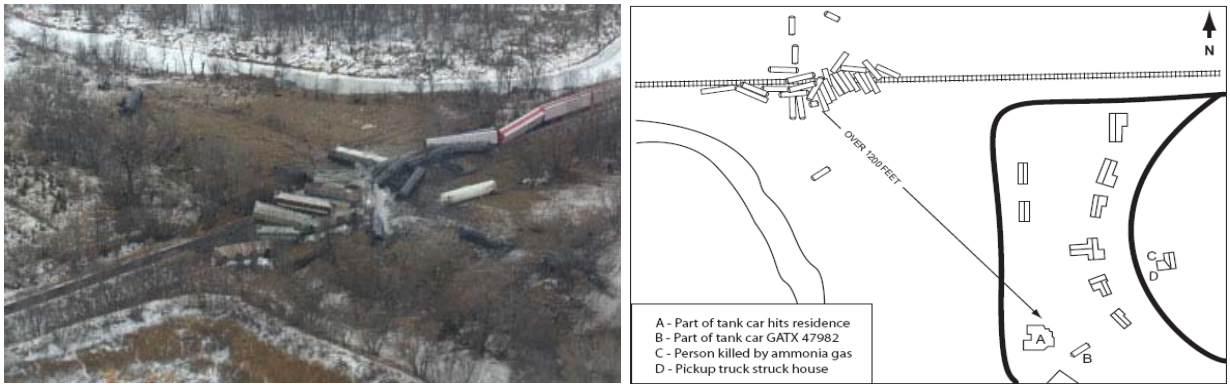

Fig. 1 - Accident scene and wreckage. Tierracita Vallejo neighbourhood (NSTB, 2004)

In the Czech Republic, accident statistics are collected by the Transport Information System of the Ministry of Transport (DOK, 2007). Since 1996 a total 27,234 of accidents were registered in all types of dangerous substances transportation in the Czech Republic. The following data from years 2002 till 2005 (the best reported years) were selected for the purpose of modelling releases and dispersion (table 1 and 2):

Table 1
Numbers of accidents in dangerous substances transportation in CZ (DOK, 2007)

Year	Road	Rail
2002	4,188	378
2003	5,394	385
2004	5,109	483
2005	5,285	456
Total 1996 - 2007	22,256	3,968

Note: These include very small leakages without consequences (e.g. valve leakage)

Table 2
Numbers of accidents caused by selected dangerous substances (DOK, 2007)

	Ammonia anhydrous		Gasoline	
Year	**Road**	**Rail**	**Road**	**Rail**
2002	36	2	725	49
2003	44	4	820	38
2004	40	9	748	85
2005	35	13	686	36
Total 1996 - 2007	284	83	3,108	2,340

As examples of other dangerous substances chlorine (total 69 accidents) and LPG – Liquefied Petroleum Gas (registered as propane – 24 accidents) were selected.

In the U.S. Department of Transportation (DOT), PHMSA - the Pipeline and Hazardous Materials Safety Administration has public responsibility for the safe and secure movement of hazardous materials to industry and consumers by all transportation modes. PHMSA revised the definition of a serious incident in 2002, and the current definition is (from the point of view road and of rail transport only): (PHMSA, 2007)

- a fatality or major injury caused by the release of a hazardous material,
- the evacuation of 25 or more persons as a result of release of a hazardous material or exposure to fire,
- a release or exposure to fire which results in the closure of a major transportation artery,
- the release of a bulk quantity (over 119 gallons or 882 pounds) of a hazardous material.

PHMSA has submitted annual statistics of transport incidents in USA. The following tables (table 3 - 5) give the most important data for comparison with the above mentioned.

Table 3
Hazardous Material Transportation Incidents in USA by Mode and Incident Year (PHMSA, 2007)

	1997	**1998**	**1999**	**2000**	**2001**	**2002**	**2003**	**2004**	**2005**	**2006**	**Total**
Air	13	25	18	35	37	15	13	6	19	17	198
Highway	397	356	447	449	488	377	399	400	418	389	4,120
Rail	61	72	68	83	63	71	58	82	84	75	717
Water	1	4	0	2	1	3	2	4	2	1	20
Total	**472**	**457**	**533**	**569**	**589**	**466**	**472**	**492**	**523**	**482**	**5,055**

Table 4
HAZMAT Summary by Result for 2006 (PHMSA, 2007)

		INJURIES			
Result	**Incidents**	**Hospitalized**	**Non-Hospitalized**	**Fatalities**	**Damage($)**
Vapour (Gas) Dispersion	467	7	31	0	16,948,674
Material Entered Waterway/Sewer	63	2	18	4	9,373,803
Spillage	19,034	22	171	5	59,455,638
Fire	54	6	3	6	8,564,879
Explosion	35	3	3	3	1,948,564
Environmental Damage	85	3	20	3	29,253,693
None	828	0	0	0	5,415,131
Total - 2006	**20,566**	**43**	**246**	**21**	**130,960,382**

Note: Due to multiple results being involved in a single incident, the total above may not correspond to the total in other reports.

Table 5
Commodity Summary by Total Injuries for Calendar Year – 2006 (PHMSA, 2007)

Rank	**Commodity Name**	**Hazard Class**	**Injuries**	**%**
1	Corrosive Liquids Toxic	Corrosive Material	50	21.55
2	Anhydrous Ammonia	Poisonous Gas	20	8.62
3	Environmentally Haz Liq	Miscellaneous Hazardous Material	16	6.90
4	Corros Liq Acidic Inorgan	Corrosive Material	8	3.45
4	Sodium Hydroxide Solution	Corrosive Material	8	3.45
6	Gasoline	Flammable-Combustible Liquid	6	2.59
6	Sulfuric Acid	Corrosive Material	6	2.59
8	Liquefied Petroleum Gas	Flammable Compressed Gas	5	2.16

8	Hydrochloric Acid Solutn	Corrosive Material	5	2.16
8	Maleic Anhydride	Corrosive Material	5	2.16
11	Paint	Combustible Liquid	4	1.72
11	Chlorine	Poisonous Gas	4	1.72
11	Silicon Tetrafluoride	Poisonous Gas	4	1.72
11	Acetic Acid Glacial	Corrosive Material	4	1.72
11	Amines Liq Corros Flam	Corrosive Material	4	1.72
11	Corros Liq Basic Inorgani	Corrosive Material	4	1.72
17	Pyridine	Flammable-Combustible Liquid	3	1.29
17	Hydrazine Aqueous Solutio	Corrosive Material	3	1.29
17	Phosphoric Acid	Corrosive Material	3	1.29
17	Sulfuric Acid >51%	Corrosive Material	3	1.29
21	Ammonia Anhydrous	Nonflammable Compressed Gas	2	0.86
21	Diesel Fuel	Flammable-Combustible Liquid	2	0.86
…	…		…	…
Total			**232**	

Argonne National Laboratory (ANL, 2000) also reports on transport risk in the USA. The purpose of this National Transportation Risk Assessment (NTRA) study was to quantitatively characterize the risks associated with the transportation of selected hazardous materials on a national basis. On the basis of the risks from TIH materials (TIH - toxic by inhalation), the results suggest that chlorine and ammonia account for 70% to 80% of the total TIH transportation risk (see Figure 2). Considering fatality risks on a per-ton-mile basis, the risks from LP gas substantially exceed the risks for gasoline, TIH, and explosives (see Figure 3).

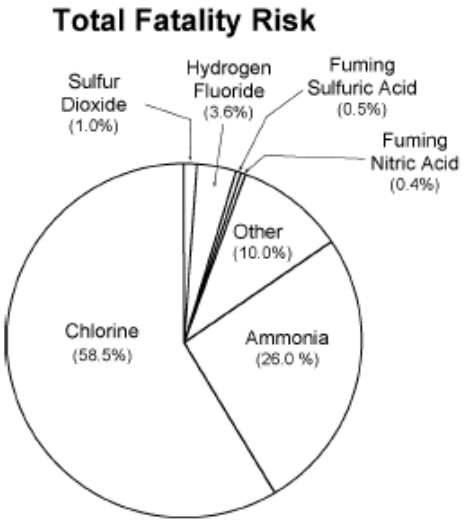

Fig. 2 - Distribution of Total TIH Fatality (ANL, 2000)

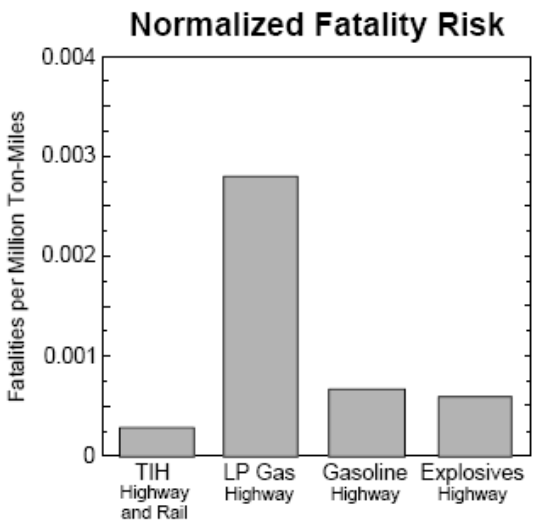

Fig. 3 - Fatalities Normalized by Commodity Flow (ANL, 2000)

3. Case study definition: Description of methodical approaches and accident scenarios

The dispersion of admixtures in the atmospheric boundary layer can be investigated on the basis of two different approaches of mathematical modelling that are as follows:

- standard (diffusion, Gaussian) models;
- CFD models (based on calculations of the system of hydrodynamic and thermodynamic equations).

In the present study, some methodologies developed in a standard way are applied to the estimation and assessment of risks associated with accidental releases of dangerous substances, and in this framework, standard software applications can be employed. For the purpose of hazardous zones modelling the following representative software packages were selected:

- ALOHA 5.4.1. [a representative of free-downloaded software from U.S. EPA (ALOHA, 2007)];
- EFFECTSGIS 5.5. [customary software of the Dutch company TNO (EFFECTS, 2004)];

– TerEx 2.7.8. [a commercially available software of the Czech company T-SOFT (TerEx, 2005)].

Generally, it might be argued that models currently used in risk assessment and evaluation of the consequences of accidents were developed to fit tasks characterized by boundary conditions and dispersion characteristics that are much more simple compared to those relevant to real urban zones. However, to obtain rough results, these models may be applied; the resulting distances of hazardous zones are then conservative, with many uncertainties in the case of obstacles present (high buildings).

After evaluating historical accidents and related statistical sources, the following hazardous substances were finally chosen as representative for modelling:

- Anhydrous ammonia – a toxic gas lighter than air;
- Chlorine – a toxic gas heavier than air;
- Liquefied Petroleum Gas (LPG) – a flammable gas;
- Gasoline – a flammable liquid.

These selected substances represent some of the most hazardous substances transported in the greatest quantities. Within this case study, two types both of road cargo tanks (MC331 High Pressure Tank, MC306 Nonpressure Liquid Tank) and rail tank cars (Pressurized Tank Cars, Nonpressurized Tank Cars) were taken into account (TRA, 1995). Traffic collisions or derailments were assumed as general scenarios of transport accidents. Two main releases of the selected substances were modelled: *instantaneous release* (in duration less than 1 min) *as the worst case scenario* (catastrophic rupture - 300 mm hole), and *semi-continuous release as an alternative scenario* representing a more probable accidental situation (50 mm hole). The severity and representative nature of the selected scenarios can be seen by comparing data released by the UK Advisory Committee on Dangerous Substances of HSC (ACDS, 1991), the U.S. Department of Transportation (US DOT, 1993) and the Argonne National Laboratory (ANL, 2000). For the purpose of real risk assessment in particular transport routes, the proposed strategy is to treat the most hazardous substances used in local industrial companies. This strategy aims to be constructive and relevant in the event of terrorist attacks.

The most important meteorological conditions influencing the dispersion of dangerous substances are direction and speed of wind, stability class and air temperature. Regarding many possibilities in real situations, the following basic conditions were finally chosen for modelling:

- The neutral stability of atmosphere [D class; medium wind speed of 5 $m \cdot s^{-1}$ (the most frequent conditions during the year → the most probable scenario)];
- The very stable stability of atmosphere [F class; low wind speed of 1.7 $m \cdot s^{-1}$ (the worst dispersion conditions, cloud impact of the largest area → the worst case scenario)].

The following Table 6 summarises all important input data necessary for modelling of releases and dispersion of the selected dangerous substances originating from road or rail transport.

Table 6
Summary of input data for modelling

Scenario No.*[1]	Dangerous substance	Amount (road/rail) [t]	Type of release	Daytime	Stability class	Wind speed [m/s]	Temperature [°C]	Level of concern [ppm] *[2]
1.1 A / B	Ammonia	15 / 50	catastrophic	day	D	5	25	7,700 (50% mort. / 30 min)
1.2 A / B				night	F	1.7	10	
1.3 A / B			continuous	day	D	5	25	
1.4 A / B				night	F	1.7	10	
2.1 A / B	Chlorine	20 / 55	catastrophic	day	D	5	25	380 (50% mort. / 30 min)
2.2 A / B				night	F	1.7	10	
2.3 A / B			continuous	day	D	5	25	
2.4 A / B				night	F	1.7	10	
3.1 A / B	LPG	10 / 24	catastrophic	day	D	5	25	12,600 (60% LEL)
3.2 A / B				night	F	1.7	10	
3.3 A / B			continuous	day	D	5	25	
3.4 A / B				night	F	1.7	10	
4.1 A / B	Gasoline	25 / 58	catastrophic	day	D	5	25	8,400 (60% LEL)
4.2 A / B				night	F	1.7	10	
4.3 A / B			continuous	day	D	5	25	
4.4 A / B				night	F	1.7	10	

Notes: *[1] *A for road, B for rail*
*[2] *from EFFECTSGIS 5.5 database*

The scenarios are described as a two-phase flow after the release of liquefied gases, followed by their dispersion. The dispersion of gasoline (a flammable liquid) was calculated by pool evaporation after the release. The fatal zones for toxic substances were modelled by a probit function employing the LC_{50} concentration for 30 min exposure. For flammable substances the fatal zones represent 60 % of LEL for a potential flash fire or vapour cloud explosion. To approximately match the multiple obstacles in cities, the highest landscape roughness was considered during all simulations.

4. Results and Discussion

Software packages ALOHA and EFFECTS represent well-known pre-accident modelling tools commonly employed in assessment of dangerous substances releases, dispersion, and other effects and consequences. A relatively new model used mainly by rescue teams in cases of accidents (post-accident modelling) has been implemented in the software package TerEx.

The following comparisons are discussed before making more general conclusions on the results obtained:

a) pre-accident versus post-accident modelling;
b) results based on ALOHA and EFFECTS software calculations;
c) the severity of catastrophic and of semi-continuous scenarios;
d) distances of hazardous zones under two types of weather conditions (the most frequent versus the worst condition from the point of view of cloud dispersion);
e) a general comparison of different results as inputs for risk assessment of the substances in question.

The results of modelling for particular substances, when used with identical data input assumptions, are summarized in the following tables (see Table 7 – 10).

Table 7
Results of modelling for ammonia

Scenario No.*[1]	ALOHA			EFFECTS			TerEx
	Release rate [kg/s]	Release duration [min]	Fatal zone [m]	Release rate [kg/s]	Release duration [min]	Fatal zone [m]	Evacuation zone [m]
1.1 A	227	1	726	1,391	0.20	681	639
1.2 A	227	1	800	1,065	0.25	280	1,830
1.3 A	13	18	175	38	6	258	647
1.4 A	9	25	236	29	8	244	3,440
1.1 B	756	1	1,300	1,390	0.50	693	1,100
1.2 B	756	1	1,400	1,068	0.75	280	3,160
1.3 B	13	59	175	38	20	258	649
1.4 B	9	60	236	29	27	244	3,450

*Notes: *[1] A for road, B for rail*

Table 8
Results of modelling for chlorine

Scenario No.*[1]	ALOHA			EFFECTS			TerEx
	Release rate [kg/s]	Release duration [min]	Fatal zone [m]	Release rate [kg/s]	Release duration [min]	Fatal zone [m]	Evacuation zone [m]
2.1 A	302	1	1,600	1,790	0.16	1,068	1,710
2.2 A	302	1	1,400	1,410	0.21	647	4,250
2.3 A	21	16	580	49	6	416	1,810
2.4 A	15	21	673	39	8	96	8,480
2.1 B	832	1	2,300	1,790	0.45	1,139	2,600
2.2 B	832	1	2,200	1,410	0.60	810	6,480
2.3 B	21	43	580	49	16	418	1,820
2.4 B	15	58	679	39	22	109	8,510

*Notes: *[1] A for road, B for rail*

Table 9
Results of modelling for LPG (propane)

Scenario No.*[1]	ALOHA			EFFECTS			TerEx
	Release rate [kg/s]	Release duration [min]	Fatal zone [m]	Release rate [kg/s]	Release duration [min]	Fatal zone [m]	Evacuation zone [m]
3.1 A	151	1	242	1,209	0.12	24	215
3.2 A	151	1	392	978	0.16	32	414
3.3 A	14	12	69	33	4	4	42
3.4 A	10	15	120	27	6	4	219
3.1 B	363	1	391	1,209	0.28	23	305
3.2 B	363	1	574	978	0.38	31	565
3.3 B	14	28	70	33	10	4	42
3.4 B	10	37	121	27	14	6	220

*Notes: *[1] A for road, B for rail*

Table 10
Results of modelling for gasoline

Scenario No.*[1]	ALOHA			EFFECTS			TerEx
	Release rate [kg/s]	Release duration [min]	Fatal zone [m]	Release rate [kg/s]	Release duration [min]	Fatal zone [m]	Evacuation zone [m]
4.1 A	20	23	37	32	3	43	48
4.2 A	6	>60	56	11	12	27	133
4.3 A	1.6	>60	10	7	24	15	22
4.4 A	1.1	>60	22	5	30	14	59
4.1 B	34	32	46	82	3	45	73
4.2 B	12	>60	86	29	11	45	200
4.3 B	1.6	>60	10	13	30	21	22
4.4 B	1.1	>60	21	3	30	20	59

*Notes: *[1] A for road, B for rail*

Employing models implemented in the EFFECTS software package, the hazardous zones calculated for chlorine tank car accidents (scenarios 2.1 B – 2.4 B) are depicted in Figure 4. As it is graphic, the software output makes a comparison of various scenarios easier, displaying different possible concentration contours in one scheme.

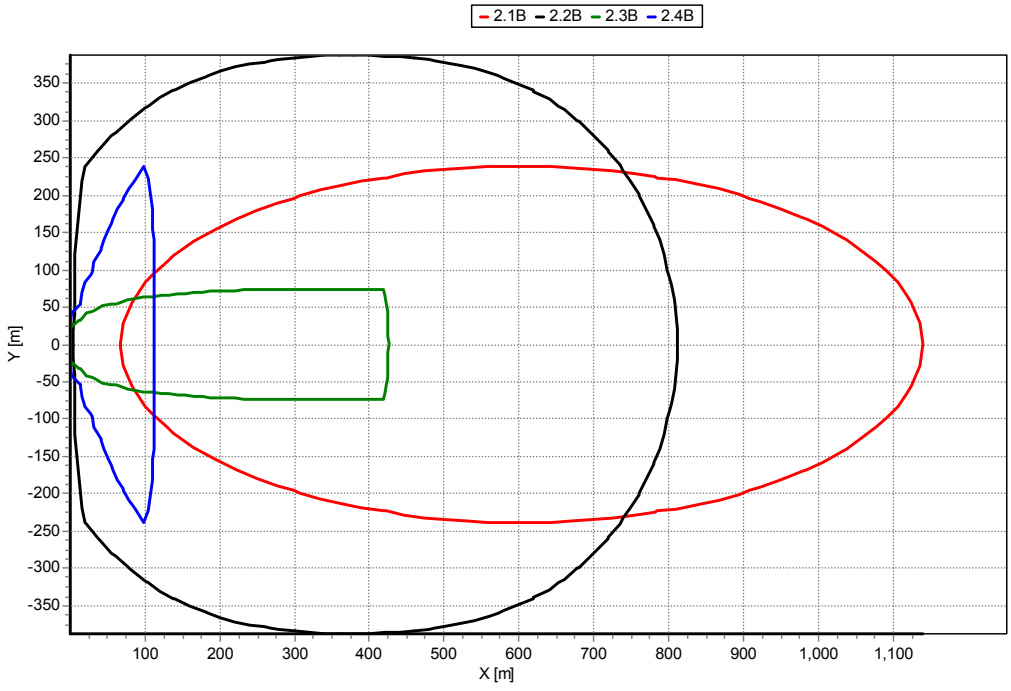

Fig. 4 – Example of modelling results for scenarios of chlorine tank car accidents, employing the graphical output of the EFFECTS software

The TerEx software package is a tool for the quick modelling needed during an emergency (post-accident modelling). For this reason, calculations can generally be done just employing a few input data. Therefore, more conservative results should also be expected. Recommended evacuation zones are derived from injury criteria (for toxic substances, e.g. IDLH) and the distances would be longer than fatal zone distances. (Note that fatality data is more certain than numbers of people harmed, but the numbers also depend on the chance distribution of people within the affected zone.) A comparison of results with pre-accident modelling is obviously possible but with caution: the main difference is that calculation speed must be kept as an essential feature of the post-accident programs, and this is generally at the expense of more detailed modelling.

The results of hazardous zones obtained by ALOHA and EFFECTS software applications are generally similar, at least of the same order. The greatest difference was for propane, where ALOHA shows the fatal zones in order of hundreds metres compared with EFFECTS in tens of metres only. However, the release rate and release durations differ more, in some cases the release rates differ 6 to 8 fold! With regard to input data identical for both software applications, the calculated release rates differ more than the distances of the hazardous zones (e.g. ammonia 1.1A: the release rate of 227 / 1391 $kg \cdot s^{-1}$ and the hazardous zones of 726 / 681 m). The program EFFECTS calculates shorter distances of fatal zones in most cases. Thus, the program ALOHA can be described as a more conservative tool from the point of view of risk assessment.

The severity of catastrophic ruptures (300 mm hole, instantaneous releases of duration less than 1 minute) is several times higher than the investigated alternative scenarios of higher probability (50 mm hole, semi-continuous releases). The clouds will reach longer and wider distances and the affected area will be much larger. Therefore, eventual casualties in densely inhabited areas will be higher too. On the other hand, the catastrophic release is less probable for common accidents. Its probability, however, could rise through terrorist attacks.

Atmospheric conditions can also have a significant influence on the cloud dispersion. Commonly, it is accepted that the cloud could reach a longer range under very stable conditions compared to neutral ones. However, most of the results based on the EFFECTS model calculations demonstrate short distances in case of obstacles (the highest surface roughness). Further calculations need to be done for a more detailed comparison.

The overall results show a high-level severity in cases of accidents within urban zones. Taking into account all the selected dangerous substances, chlorine could cause the largest fatal zone. When considering road or rail transport accidents, the radius of affected zone is up about 1 km. The results of ammonia dispersion modelling are characterized by a shorter radius of the order of hundreds of metres. Propane and gasoline, the flammable substances, are dispersed so that explosive (or flammable) mixtures can be expected close to the release source only (i.e. up to a distance of a few hundred metres for propane, and about 50 m for gasoline). For purely accidental releases the total severity of these accidents must be judged together with the frequencies in inhabited areas. For example, a chlorine accident has high severity and lower probability compared to a gasoline accident with low severity and higher probability.

5. Environmental aspects of accidental releases originating in transport of dangerous substances

In major accidents of stationary and mobile risk sources (fires, explosions and toxic releases) a large quantity of gaseous pollutants and/or aerosols come into the troposphere, producing significant air pollution. Furthermore, accidental releases of dangerous substances can subsequently influence other environmental systems and sub-systems. Thus for transport accidents, the environmental fate of the evaluated compounds has also been reviewed. The results are discussed below reflecting the knowledge base currently available by a literature search.

A m m o n i a

Ammonia evaporates at temperatures above –33°C and will transport over several kilometres as a gas. It readily forms ammonium sulphate particles when sulphur compounds occur in air: these particles then can be transported over hundreds of kilometres in plumes. Of all atmospheric ammonia reactions known, one of the most important seems to be that involving conversion of ammonia to ammonium (NH_4^+) particulate (PSLAR, 1999):

$$NH_2HSO_3 + NH_3 \Leftrightarrow NH_2 \cdot SO_3NH_4 \qquad (1)$$

This conversion occurs in the lowest 100 m of the atmosphere at rates ranging from $1x10^{-3}$ s^{-1} to $5x10^{-5}$ s^{-1} (this is a first-order reaction, which means the reaction rate is dependent on the concentration of one reactant, namely NH_3), and daytime conversion is much faster than that at night. The reaction is dependent on temperature, relative humidity and pH. All studies conveyed the opinion that the main factors obstructing a long-range transport of ammonia in the atmosphere, both vertically and horizontally, are a rapid conversion to ammonium aerosol and the relatively high dry deposition velocity of ammonia. Because of rapid reaction rates of ammonia in air, anything between 56 % and 94 % of atmospheric ammonia is converted to ammonium particulate/ammonium aerosol. Over oceans, ammonium particulate/ammonium aerosol has an estimated atmospheric residence time of 22 hours; over land, the estimated residence time is in the range of 7–19 days. In comparison, the estimated residence time of atmospheric NH_3 is 3.6 hours over oceans and in the range of 2.8 hours to 4 days over land. These short residence times are primarily due to the rapid conversion to ammonium particulate/ammonium aerosol and the high dry deposition velocities of ammonia. Ammonia is not involved in the formation of ground-level ozone, the depletion of stratospheric ozone or climate changes (PSLAR, 1999).

In the atmosphere, ammonia may undergo many transformations; the most important removal mechanism is represented by dissolution in water droplets, which can subsequently be removed by rain or washout. Ammonia can also be removed by reaction with OH radicals. In soil, the most likely fate of ammonia is its conversion to nitrates through the nitrification action of micro-organisms. Nitrates are in turn lost from soils by leaching, denitrification and uptake by the plant root systems. In natural waters, ammonia can be removed by bacteria through nitrification, assimilation by aquatic algae and macrophytes, adsorption on particulates and subsequent sedimentation, and volatilization. These processes contribute to the natural cycling of nitrogen in the environment, and help to prevent the persistence and accumulation of elevated levels of ammonia. Studies describing toxicological effects of ammonia on wildlife are limited, as ammonia occurring in the atmosphere at common concentration levels is not usually harmful to animals. It has been suggested that non-ionized ammonia (NH_3) represents a primary toxic specie to fish (OSA, 2001). Ammonia can also reach toxic concentrations during transport accidents near forests or remote areas.

C h l o r i n e

Chlorine exists as a greenish-yellow gas under standard conditions (25°C and pressure of 1 atm), or as a high-density amber liquid when compressed. Information regarding the environmental fate of chlorine in air was not found in the secondary sources searched. Since chlorine is converted to HCl in the atmosphere, prevailing meteorology strongly determines the fate of HCl in the atmosphere. However, HCl is not considered as a strongly persistent pollutant or one where long range transport is important in predicting its ecological effects. In the atmosphere, HCl can be expected to be absorbed into aqueous aerosols, due to its great affinity for water, and removed from the troposphere by rainfall. In addition, HCl will react with hydroxyl ions to yield water plus chloride ions (EPA, 1994).

Chlorine may react with soil components to form chlorides; depending on their water solubility, these chlorides are easily washed out from the soil. Chlorine hydrolyses very rapidly in water (rate constants range from $1.5x10^{-4}$ s^{-1} at 0°C to $4.0x10^{-4}$ s^{-1} at 25°C; the half-life in natural waters is approximately equal to 0.005 s). In fresh- and wastewaters at pH >6, complete hydrolysis occurs with the formation of hypochlorous acid (HOCl) and chloride ion (Cl^-). The hypochlorous acid ionizes to hydrogen ion (H^+) and hypochlorite ion (OCl^-). Vaporization of molecular chlorine (Cl_2) from water to the atmosphere may be significant at low pH values and high concentrations (e.g., pH=2 and 3500 $mg{\cdot}l^{-1}$ chlorine), but is insignificant at neutral pH and low concentrations. There is no potential for the bioaccumulation or bioconcentration of chlorine, but chlorine has high acute toxicity to aquatic organisms (EPA, 1994).

L P G

Liquefied petroleum gas primarily comprises propane and butane, so the physical properties of a specific commercial LPG will depend on the relative proportions of its constituents (e.g. in the UK, LPG typically consists of 90 % propane). LPG is denser than air and thus will accumulate in places such as drains, trenches or other depressions. The high vapour pressures of propane and butane suggest that almost all of any LPG released will enter the atmosphere. Propane and butane in the atmosphere are degraded by reaction with photo-chemically produced hydroxyl radicals. The reaction with hydroxyl radicals under the influence of sunlight is estimated to result in half-lives of 13 days for propane and 6 days for butane. The Henry's Law constants (0.7067 $atm{\cdot}m^3{\cdot}mol^{-1}$ for propane; 0.9497 $atm{\cdot}m^3{\cdot}mol^{-1}$ for butane) suggest rapid volatilisation from aquatic environments. These hydrocarbons are not sensitive to hydrolysis under environmental conditions but are considered readily biodegradable.

Bioconcentration factors have been estimated for propane to range from 1.56 to 1.78 and those for butane from 1.78 to 1.79; thus bioconcentration is not an important factor influencing organisms in aquatic systems. Estimated K_{oc} values ranging from 450 to 460 in case of propane, or 450 to 900 in case of butane, respectively, indicate that some of the primary constituents of LPG may partition from water column to organic matter contained in sediments and suspended materials. However, volatilisation is expected to be the dominant rate process (ETSU, 2000).

G a s o l i n e

Gasoline is a complex mixture of hydrocarbon compounds which have differing properties and therefore different behaviours in the environment. If released to the open environment, the majority of compounds present in gasoline will evaporate to the atmosphere where they will be degraded by reaction with hydroxyl radicals in a matter of days. Because gasoline floats on water, it may be carried for long distances from initial source by water courses, sewers, drains or groundwater. The majority of gasoline released to soil will be biodegraded. The range of log K_{ow} values for gasoline compounds (those with log K_{ow} > 4) suggests that a number of compounds found in gasoline will have the potential to bioaccumulate significantly in aquatic and/or terrestrial organisms (ETSU, 2000).

The summary of impacts of the evaluated substances on the main environment compartments is shown in the following Table 11.

Table 11
Environmental compartments affected by evaluated substances

Dangerous substances	Environmental compartment		
	Air	Water	Soil
Ammonia	+	+	-
Chlorine	+	+	-
LPG	+	-	-
Gasoline	+	+	+

+ Significant effects
- No significant effects

Environmental damage caused by accidents from dangerous substances transport depends mainly on the specific location of the accident and on the substance state of matter. For example, if an accident with liquids or liquefied gases occurs near surface water, then water will represent the most influenced environmental compartment. Similarly, most of a dangerous substance would probably be evaporated to air if the location of accident is on an impervious hard surface. In the atmosphere, the humidity also plays an important role - differences can appear in zones affected by vapour clouds under rainfall and dry weather conditions. Water drops could wash out vapour from the air, contaminating soil or surface water (e.g. the Seveso accident in 1976). Generally, it can be stated that the atmosphere represents the main transfer medium for released substances to enter other environmental compartments (biota, soil, and surface water). The topography of the accident location is another factor which will significantly influence the range of dispersed cloud.

6. Discussion

It should be noted that standard software either neglects humidity and topography, or is relatively insensitive to variations in them. Therefore these conditions should be explored by wind tunnel experiments and CFD modelling.

While risk assessment of dangerous substances during transport is covered by general safety laws, there are as yet no European laws which require sites to consider the external transport of products and raw materials as part of their general operation. The Seveso II directive covers only internal transport of dangerous substances inside industrial companies, but external transport can be more dangerous to people and the environment. In addition, the methodology of transportation risk assessment is not as developed in scope as for stationary risk sources. The best known methodologies are only three guidelines, the Major Hazard Aspects of the Transport of Dangerous Substances of HSE (ACDS, 1991), the Transportation Risk Analysis of AIChE (TRA, 1995) and Dutch methodology in publication “Purple Book” (TNO, 1999). Consequence evaluation is an important part in risk assessment even if the results often contain many uncertainties. A method to identify and quantitatively evaluate such uncertainties would be to carry out a comparative study of mathematical diffusion models and computational fluid dynamics (CFD) models of the same scenario. In addition, physical modelling employing an appropriate wind tunnel should be applied to obtain data which is

most relevant. Because CFD modelling as well as wind tunnel experiments are expensive and time-consuming approaches, the results of the assessments which have been reported above can serve as a basis for preparing such simulations,. The aim is the investigation of the limitations of standard models, and possible ways of their improvement, respectively. These sub-goals also represent the first step necessary for building up a more comprehensive step-by-step methodology generally applicable to assessment of mobile risk sources.

7. Conclusion

At present, the estimation of consequences of accidents of mobile risk sources is carried out rather sporadically, usually employing simple mathematical models. The models used only give indications of hazardous zones following the release and dispersion of dangerous substances in densely inhabited areas. Nevertheless, the determination of hazardous zones is important to evaluate the possible consequences of major accidents or terrorist attacks. A critical comparison of existing methods has been carried out as the basis for further study. Model releases and dispersion of dangerous gases (or vapours) in cases of major accidents of road and rail transportation in urban zones have been investigated and their possible consequences discussed in our contribution.

The ultimate aim of this project is to provide practical help in the assessment of risks related to the transport of dangerous substances and stationary risk sources located in built-up and inhabited areas. The results could be useful for various studies of acute and chronic risks and/or environmental risks related to accidental releases into the atmosphere, when measures for prevention or mitigation are to be proposed. For example, this may influence the location of ventilation intakes in buildings located near a possible accident site (fixed or transport). It may be possible to make better comparisons of possible transport routes of dangerous substances in terms of the likely outcome of an accident.

Finally, our results can be employed when preparing more sophisticated simulations based on computational fluid dynamics modelling and wind tunnel experiments, and aimed at investigation of the limitations of standard models on one hand, and their improvement on the other hand.

Acknowledgement
A part of this work was carried out in the framework of the ESF-programme INTROP (Exchange Grant no. 1404). This study was also supported by the Czech Ministry of Education within the frame of the EU COST 729 Action (Grants no. OC 111, and OC 186).

References

ACDS, 1991. Major hazard Aspects of the Transport of Dangerous Substances, Health and Safety Commission, Advisory Committee on Dangerous Substances, HMSO, London, ISBN 0118856766

ALOHA, 2007. CAMEO ALOHA, U.S. EPA, downloading from http://www.epa.gov/ceppo/cameo/aloha.htm.

ANL, 2000. A National Risk Assessment for Selected Hazardous Materials in Transportation, by D.F. Brown, W.E. Dunn, and A.J. Policastro, Argonne National Laboratory, Illinois, ANL/DIS-01-1

Dharmavaram S. and Hanna S. R., 2007. Computational Fluid Dynamics (CFD) Modelling of Toxic Gas Dispersion in the Vicinity of Complex Buildings, Structures, and Topography, In *12th International Symposium Loss Prevention and Safety Promotion*, Edinburgh, UK, 22.-24.5. 2007, paper 043

DOK, 2007. Ministry of Transport of the Czech Republic, Transport Information System DOK (Dopravní informační system), http://cep.mdcr.cz/dok2/DokPub/dok.asp

EFFECTS, 2004. Program EFFECTSGIS 5.5., TNO Environment, Health and Safety, Netherlands, www.mep.tno.nl.

EPA, 1994. Chemical Summary for Chlorine, U.S. Environmental Protection Agency, Office of Pollution Prevention and Toxics, EPA 749-F-94-010a, http://www.epa.gov/opptintr/chemfact/s_chlori.txt

ETSU, 2000. Health and Safety of Competing Fuel Options For Fuel Cells in the Road Transport Sector, ETSU F/03/00210/00/REP, MRC Institute for Environment and Health, http://www.consumer.gov.uk/renewables/publications/pdfs/f0300210.pdf

McBride M.A., Reeves A.B., Vanderheyden M.D., Lea C.J., Zhou X.X., 2001. Use of Advanced Techniques to Model the Dispersion of Chlorine in Complex Terrain, In *Process Safety and Environmental Protection,* 79 (B2): March 2001, pp. 89-102, ISSN: 0957-582.

NTSB, 2004. Derailment of Canadian Pacific Railway Freight Train 292-16 and Subsequent Release of Anhydrous Ammonia Near Minot, North Dakota, January 18, 2002. National Transportation Safety Board, Railroad Accident Report NTSB/RAR-04/01. Washington, DC.

Oggero A., Darbra R.M., Mu˜noz M., Planas E., Casal J., 2006. A survey of accidents occurring during the transport of hazardous substances by road and rail, In *Journal of Hazardous Materials,* A133, 1–7

OSA, 2001. ONTARIO STANDARDS AIR FOR AMMONIA, March, 2001 Standards Development Branch Ontario Ministry of the Environment, http://www.ene.gov.on.ca/envision/env_reg/er/documents/2001/airstandards/pa00e0003.pdf

PHMSA, 2007. U.S. Department of Transportation, Hazardous Materials Information System, Data as of 04/02/2007, http://www.phmsa.dot.gov/

PSLAR, 1999. PRIORITY SUBSTANCES LIST ASSESSMENT REPORT, Ammonia in the Aquatic Environment, Canadian Environmental Protection Act, Minister of Public Works and Government Services Canada 2001, ISBN 0-662–29192–1

TerEx, 2005. Program TerEx 2.7.8., T-SOFT, Czech Republic, http://www.tsoft.cz/index.php?q=cz/terex

TNO, 1999. Guidelines for Quantitative Risk Assessment, “Purple Book”, CPR 18E , TNO, The Hague.

TRA, 1995. Guidelines for Chemical Transportation Risk Analysis, Center of Chemical Process Safety of the American Institute of Chemical Engineering, New York, ISBN 0-8169-0626-2.

US DOT, 1993. Hazardous Materials Transportation in Tank Cars: Analysis of Risks, by Phani K. Raj and Clayton K. Turner from Technology & Management Systems, Inc., U.S. Department of Transportation, Report No. FRA/ORD-92/34